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Combustion Synthesis of Ceramic-Metal Composites

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# THE EFFECT OF GRAVITY ON THE IN-SITU COMBUSTION SYNTHESIS OF CERAMIC-METAL COMPOSITES

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## Abstract

This paper describes the effect of gravity on the application of combustion synthesis reactions which deliberately generate liquids and gaseous species at the reaction front. The effect of gravity-driven fluid flow and vapor phase transport on the resultant microstructure and phase morphology of the product composite materials is discussed.

## Introduction

Combustion synthesis,<sup>1,2</sup> or self-propagating high temperature synthesis (SHS) provides an attractive, affordable alternative to the conventional methods of producing advanced materials such as advanced ceramics, ceramic-composites and intermetallic compounds. The underlying basis of combustion synthesis relies on the ability of highly exothermic reactions to be self sustaining and, therefore, energetically efficient. The exothermic SHS reaction is initiated at the ignition temperature,  $T_{ig}$ , and generates heat which is manifested in a maximum or combustion temperature,  $T_c$ , which can exceed 3000K. Such high combustion temperatures are capable of melting and/or volatilizing low melting and boiling point reactants and products. This can provide both advantages and disadvantages with respect to synthesizing new high performance materials. The generation of such liquid and/or gaseous species at and ahead of the reaction front will affect the stability of the combustion synthesis reaction and will be influenced by the extent of gravity acting on them.

The exothermic reactant mixture, normally in the form of powders, is pressed into a pellet of a certain green density and is subsequently ignited, either locally at one point (propagating mode) or by heating the whole pellet to the ignition temperature of the exothermic reaction (simultaneous combustion mode). A schematic representation of a typical temperature-time plot

for a combustion synthesis reaction is given in Figure 1. The unreacted mixture ahead of the reaction front, at initial temperature,  $T_0$ , is heated to the ignition temperature,  $T_{ig}$ , whereupon the reaction is initiated.

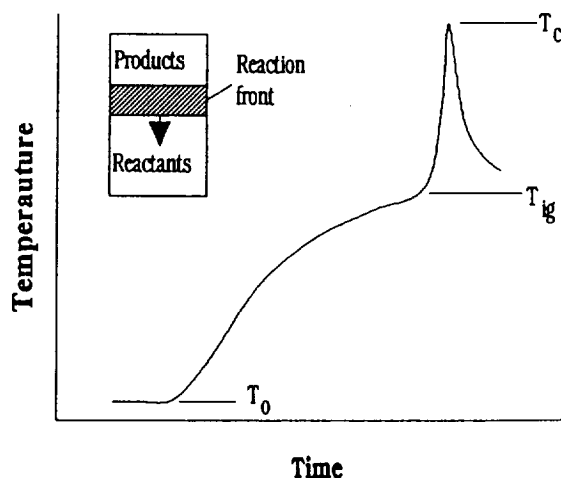


Fig. 1. Schematic representation of the temperature-time curve during a SHS reaction.

Sufficient heat is released by the exothermic reaction, as indicated in Figure 1, in order to sustain the reaction throughout the pellet. In the propagating mode the reaction propagates through the pellet via a reaction zone of width  $\delta w$ . This reaction zone is the zone over which most combustion synthesis reactions are initiated and completed, and therefore, the thickness of the zone is defined by the degree of completion of the reaction,  $\eta$ , from zero to one. The rate of the reaction,  $\phi$ , will be a maximum at some position within the combustion zone,  $\delta w$ , as indicated in Figure 2.<sup>1</sup> The initial,  $T_0$ , ignition,  $T_{ig}$ , and combustion,  $T_c$ , temperatures are also indicated in this diagram as is the direction and velocity,  $V$ , of the propagating reaction front. This is an idealized schematic representation, since in some cases the reaction is not completed within the reaction zone and can continue in what is called "an afterburn".

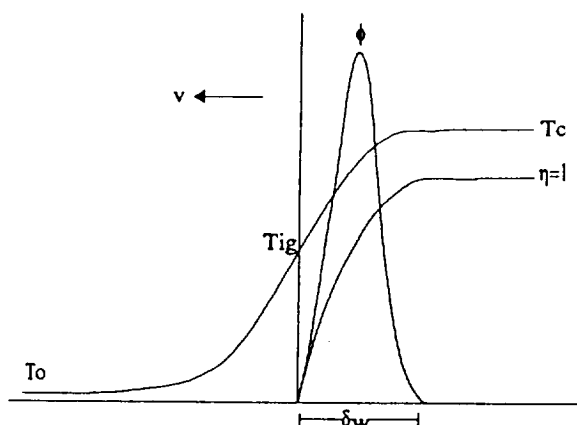
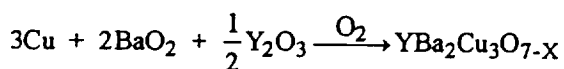


Fig. 2. Schematic representation of the reaction parameters for a propagating combustion wave.<sup>1</sup>

In the latter case, the degree of completion of the reaction,  $\eta$ , continues to increase for some period and distance outside of  $\delta w$ .

Over 500 compounds have been synthesized using combustion synthesis reactions.<sup>3</sup> These range from simple elementary reactions such as:  $\text{Ti} + \text{C} = \text{TiC}$ ;  $\text{Ni} + \text{Al} = \text{NiAl}$ ; to more complex thermite-like reactions:

i.e.  $3\text{TiO}_2 + 3\text{C} + 4\text{Al} = 3\text{TiC} + 2\text{Al}_2\text{O}_3$  and have also included the synthesis of high temperature superconducting materials, i.e.



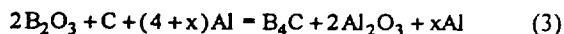
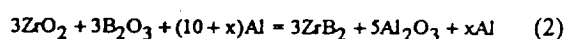
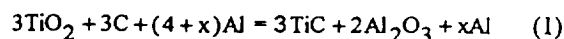
The main reaction parameters<sup>4</sup> that control these combustion synthesis reactions can be listed as the exothermicity of the reactants and products which is also associated with the reaction stoichiometry, particle size, the use of diluents or inert reactants, green density, and pre-heating of the reactants. Each of these reaction parameters will affect the exothermicity of the reaction and, as such, will affect the control of the combustion and ignition temperatures, thereby affecting the microstructure and morphology of the products and the resulting properties of the synthesized materials.

The high combustion temperatures produced in these SHS reactions are often sufficient to generate liquid and gaseous species at or ahead of the reaction front. Such species will be subject to gravity-driven fluid flow and vapor transport which are likely to significantly affect both the SHS reaction stabilities and morphology of product

phases. Therefore, this research program was aimed at investigating the effect of gravity on such SHS reactions.

### Experimental Procedure

Three reaction systems were selected to provide a suitable range of liquid and gaseous front and which would be expected to be affected species generated at, and ahead of the SHS reaction by gravity, i.e.



The reactant powders were mixed according to the required stoichiometric ratios for the three different reaction systems investigated in this research program. The important physical properties of the reactants and products used in these systems are presented in Table I.

Table 1. Properties of the materials used in the reaction systems.

Material	Melting Point T <sub>mp</sub> (°C)	Boiling Point T <sub>bp</sub> (°C)	Density (g/cm <sup>3</sup> )
TiO <sub>2</sub>	1830	3000	4.26
C			2.25
Al	660	2467	2.70
TiC	3140	4820	4.93
Al <sub>2</sub> O <sub>3</sub>	2050	2980	3.97
B <sub>2</sub> O <sub>3</sub>	450	1860	2.46
ZrO <sub>2</sub>	2715	5000	4.56
ZrB <sub>2</sub>	3000		6.09
B <sub>4</sub> C	2450	3500	2.52

Each reaction system was varied with respect to stoichiometry, i.e.  $x\text{Al}$ , pressed at 10,000 psi (68.9 MPa) into pellets of 13mm dia by 25mm in length and ignited in a specially designed reaction chamber (Figure 3). A minimum of three reaction pellets were used for each reaction stoichiometry and gravity condition, i.e. 0.01g, 1g, 2g. These reaction systems, green densities and pellet dimensions were selected from experience of the optimum conditions previously determined for these combustion synthesis reactions.<sup>5</sup> Each of

these combustion synthesis reactions are capable of producing ceramic-metal composites when  $x_{Al}$  exceeds zero. Under these conditions, the reactant Al becomes liquid (melting point  $660^{\circ}\text{C}$ ) prior to the ignition temperature ( $700\text{--}1000^{\circ}\text{C}$ ), and the generated liquid Al will be influenced by gravity-driven fluid flow.<sup>5</sup> The combustion temperatures generated in reaction (1) are sufficient to melt  $\text{Al}_2\text{O}_3$  (melting point  $2050^{\circ}\text{C}$ ) but insufficient to produce significant partial pressures of Al. The inclusion of  $\text{B}_2\text{O}_3$  as a reactant in reactions (2) and (3) provides a second low melting point reactant which also generates a high vapor pressure, i.e.  $>1$  atmosphere, at the reaction front. In addition, for reaction (2), the combustion temperatures generated by this exothermic reaction are sufficient to provide considerable vapor pressures, e.g.  $10^{-2}$  at, of Al.<sup>5</sup> On the other hand, the combustion temperatures generated in reaction (3) were sufficiently low to avoid significant vaporization of Al.<sup>5</sup> Hence, reaction (2) provided liquid Al, liquid  $\text{B}_2\text{O}_3$  and a large volume of gaseous  $\text{B}_2\text{O}_3$  at a high vapor pressure, i.e.  $>1$  at. Therefore, each of these reactions, depending on the reaction stoichiometry, provided a suitable range of liquid and gaseous species at and ahead of the reaction front conducted in the propagating mode.

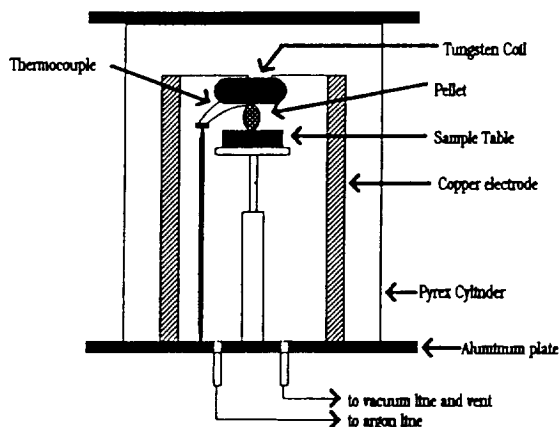


Fig. 3. Schematic of the reaction chamber used for initial combustion synthesis reactions.

The combustion synthesis reactions were ignited using a flat tungsten coil positioned between two electrodes and heated to maximum temperature using a Sorensen DCR 40-70B power (28V, 80A) supply or an equivalent power supply in the NASA Lear Jet. An adjustable graphite table with copper support was used to allow different sized pellets to be aligned in a desired location. The graphite table was tapered to

minimize the contact with the pellet and to minimize heat conduction through the bottom of the pellet. A pellet support device was constructed with threaded rod, a steel block ( $0.5'' \times 0.5'' \times 0.25''$ ) and a ceramic thermocouple insulator which was used to hold the pellets in place as well as to ensure proper placement of the thermocouples on the top surface of the pellets. These chambers were also designed with a pressure relief valve (Swagelok 4CPA-3), adjustable from 3 to 50 psi, to prevent a pressure buildup which could result in catastrophic failure of the reaction chamber.

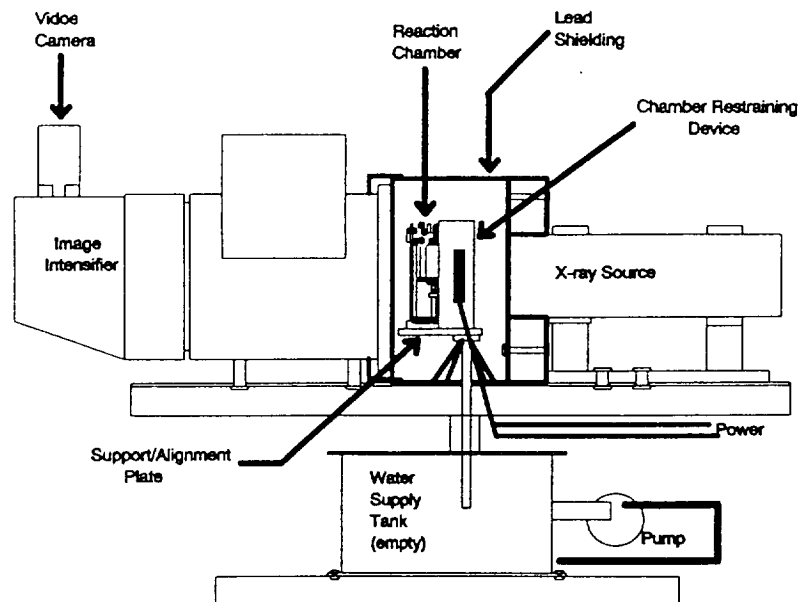
Ignition and combustion temperatures were recorded using tungsten-5% rhenium vs. tungsten-26% rhenium thermocouples interfaced to a strip chart recorder to allow time - temperature measurements. A two wavelength optical pyrometer (Iacon MR-OR15-350) was also used for all ground based experiments.

Reactions were recorded on a video camera to allow for subsequent analysis of the reaction speeds and stabilities. The low gravity combustion synthesis reactions were conducted in the NASA - LeRC Lear Jet. The experiments were also monitored by a real time x-ray radiography video unit under normal (1g) gravity conditions, reduced gravity conditions (0.01g), and increased (2g) gravity conditions. The experimental arrangement is presented in Figure 4. This allowed the combustion front to be examined without any interference from the volatiles or the brightness of the reaction front and also provided important information on the real time formation of porosity at, ahead of, and behind the reaction front.

The minimum acceleration environment (equal to an acceleration on the order of 0.01 earth's gravity) is attained by flying the aircraft through a Keplerian trajectory (Figure 5). The maneuver is entered from a slight dive requiring a 2 to 2.5 g pull-up just prior to achieving microgravity conditions, i.e. 0.01g, in the trajectory. The maneuver is terminated with a similar pull-up to a level flight path. A maximum of six trajectories can be flown before for each flight. This is due to inherent lubrication limitations of the aircraft for these flight conditions.

Samples reacted in 1g conditions were placed in three possible orientations, as shown in Figure 6, to facilitate examination of the effect of gravity. The  $\text{B}_4\text{C-Al}_2\text{O}_3\text{-Al}$  reaction (3) was oriented as

(a)



(b)



Fig. 4. (a) Schematic diagram and (b) photograph of the real time x-ray radiography system used for conducting combustion synthesis reactions in the NASA Lear Jet.

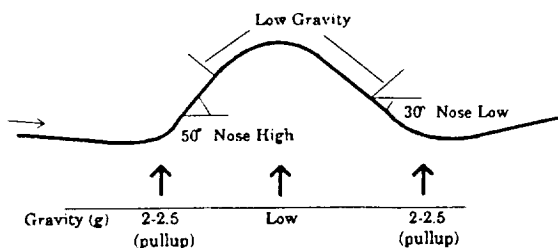


Fig. 5. Schematic representation of the Keplerian trajectory used in the NASA Lear Jet.

shown in Figure 6 to allow for the expansion of the product that occurred in this reaction system. All reactions in 0.01g or 2g conditions were oriented in the standard orientation.

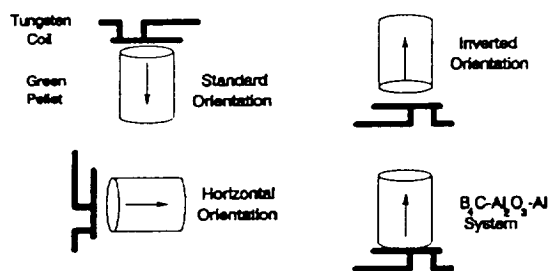


Fig. 6. Schematic diagram illustrating orientations of the pellet with respect to the tungsten coil. The arrow indicates the direction of the propagating reaction.

## Results and Discussion

### TiC-Al<sub>2</sub>O<sub>3</sub>-Al composite system - reaction (1)

The effects, of sample, orientation reaction stoichiometry (xAl) and gravity on the ignition,

Tig, and combustion, Tc, temperatures and propagation velocity, V, are presented in Table II. Increasing the excess amount of Al, i.e. xAl, increased Tc, decreased Tig, and increased the velocity of the propagating wave under normal (1g) gravity conditions. Increasing xAl will provide an increased amount of liquid Al which can permeate the voids in the reactant mixture, improve the reactant contact and can result in an earlier (lower temperature) ignition of the combustion synthesis reaction. This increase in excess Al will also provide an increased heat sink in the reactant mix and decrease the heat loss from the reaction front resulting in increased combustion temperatures. The resulting higher combustion temperatures, Tc, also result in increased propagation velocities, V, according to the simplified relationship:

$$V^2 = f(n) \frac{c\rho kRT_c^2}{QE} K_0 \exp\left(\frac{-E}{RT_c}\right) \quad (4)$$

where  $f(n)$  is a function of the order,  $n$ , of the reaction,  $c$ ,  $\rho$  and  $k$  are the heat capacity, density and thermal conductivity respectively of the product(s),  $K_0$  is a constant,  $Q$  the heat of the reaction,  $R$  the gas constant,  $E$  the activation energy for the combustion synthesis reaction when is under Arrhenius kinetics control.

The orientation of the pellet did not appear to affect Tig or Tc, but pellets reacted in the inverted orientation exhibited the highest propagation velocities, while those reacted in the normal or standard orientation exhibited the lowest velocities. It appears, therefore, that there is a gravitational effect on V, since those pellets reacted in the inverted orientation propagate with the aid of

Table II - Ignition and combustion temperatures for the TiC-Al<sub>2</sub>O<sub>3</sub>-Al reaction system.

System	rientation	1 g			2 g			0 g		
		Tig	Tc	V	Tig	Tc	V	Tig	Tc	V
		°C	°C	mm/s	°C	°C	mm/s	°C	°C	mm/s
TiC-Al <sub>2</sub> O <sub>3</sub> -Al x=0	normal	1380	1869	1.88	1376	1873	2.07	1377	1880	1.84
	horizontal	1376	1872	2.18	-	-	-	-	-	-
	inverted	1385	1875	2.29	-	-	-	-	-	-
TiC-Al <sub>2</sub> O <sub>3</sub> -Al x=4	normal	1236	1965	2.41	1240	1961	2.96	1242	1968	2.41
	horizontal	1240	1968	2.82	-	-	-	-	-	-
	inverted	1238	1963	3.23	-	-	-	-	-	-
TiC-Al <sub>2</sub> O <sub>3</sub> -Al x=9	normal	1207	2011	-	1209	2000	-	1211	2000+	-
	horizontal	1211	2007	-	-	-	-	-	-	-
	inverted	1204	2019	-	-	-	-	-	-	-

gravitational forces while those reacted in the standard orientation propagate against gravitational forces. Since Tig and Tc were largely unaffected by orientation, this velocity effect with orientation can be presented solely as a gravitational effect.

However, there were significant differences in the macrostructure and microstructure of the products with respect to gravity. The macrostructures presented in Figure 7, for reaction stoichiometries of  $x = 4$ , indicate that the porosity is more uniform and finer for those reactions conducted in microgravity compared with reactions conducted under 1g conditions. At the same time, the long radial pores tend to be smaller and the excess Al more uniformly dispersed in the sample reacted under microgravity conditions. This is clearly the result of the absence or minimization of any gravity-driven fluid (liquid Al) flow producing a more uniform distribution of Al and microstructure. The finer pore structure becomes more evident at higher magnifications [Figure 7(c) and (d)]. At even higher magnifications the effect of microgravity processing conditions reveal the formation of a fine Al network surrounding the fine TiC and  $Al_2O_3$  particles evident for products synthesized under microgravity conditions [Figure 7(f)] with no such Al network being present for products synthesized under normal gravity (1g) conditions [Figure 7(e)]. This refinement of microstructure in samples reacted under microgravity conditions becomes more evident on increasing the amount of excess Al as indicated in Figures 7(g) and (h).

#### ZrB<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-Al Composite System - Reaction (2)

The effects of sample orientation, reaction stoichiometry (xAl) and gravity on Tig, Tc and V

are presented in Table III. Similar trends are observed as those discussed for the TiC-Al<sub>2</sub>O<sub>3</sub>-Al reaction (1) system: increasing xAl decreases Tig, increases Tc and increases V; V increased with orientation in the order standard orientation, horizontal orientation, inverted orientation. Similar explanations used for the TiC-Al<sub>2</sub>O<sub>3</sub>-Al system can be involved for the ZrB<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-Al with respect to these trends. However, there appears to be less dependence of the propagation velocity on gravity in this ZrB<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-Al system compared with the TiC-Al<sub>2</sub>O<sub>3</sub>-Al system.

Video camera recordings of this reaction conducted in the horizontal orientation under normal (1g) conditions are given in the form of four photographs in Figure 8 in the form of four frames from the recording. It is clearly evident that Al has melted ahead of the reaction front and formed a liquid Al droplet underneath the pellet, clearly indicating the effect of gravity-driven liquid Al flow occurring in this reaction system.

Differences in macrostructure and microstructure were also evident in this reaction system for samples reacted in normal and microgravity conditions. Again, a more uniform distribution of the excess aluminum and porosity were evident in those samples reacted in microgravity [Figure 9(a)] compared with those reacted in normal (1g) gravity conditions [Figure 9(b)] - note the excess Al segregating to the bottom of the sample ( $x = 9$ ) in Figure 9(b) compared with a more uniform distribution of Al in Figure 9(c). In addition, the fine Al network surrounding the fine ZrB<sub>2</sub> and  $Al_2O_3$  particles are again evident for samples reacted under microgravity conditions [Figure 9(c)] and absent for samples reacted under 1g conditions [Figure 9(d)].

Table III - Ignition and combustion temperatures (°C) for the ZrB<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>- Al reaction system.

System	Orientation	1 g			2 g			0 g		
		Tig	Tc	V	Tig	Tc	V	Tig	Tc	V
				mm/s			mm/s			mm/s
ZrB <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub> -Al	normal	1407	2025	.50	1401	2000+	0.99	1411	2000+	.46
x=0	horizontal	1410	2021	.54	-	-		-	-	
	inverted	1404	2029	.59	-	-		-	-	
ZrB <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub> -Al	normal	770	2130		768	2000+		776	2000+	
x=9	horizontal	763	2122		-	-		-	-	
	inverted	772	2142		-	-		-	-	

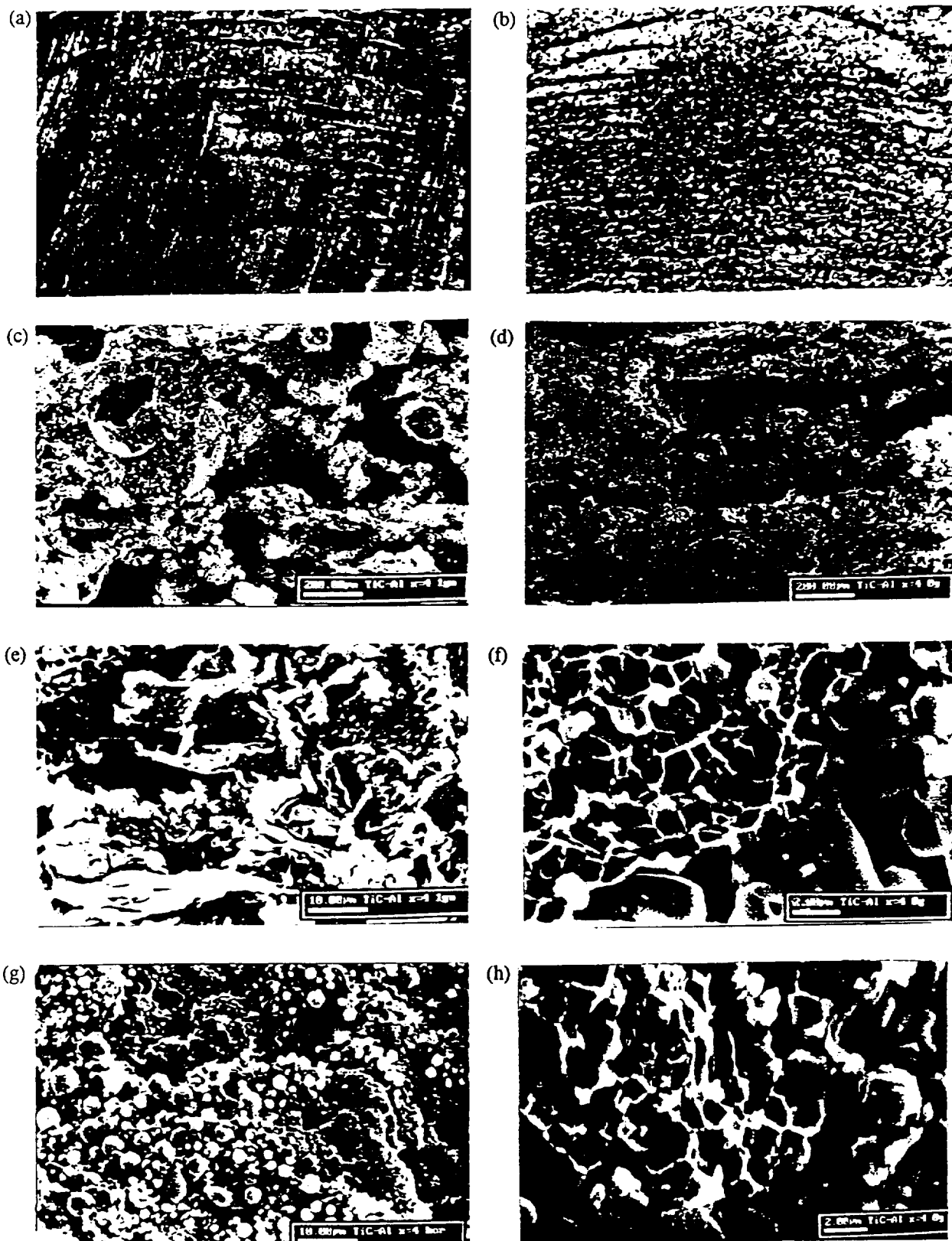


Fig. 7. Macrostructures and microstructures of products from reaction (1) for a reaction stoichiometry of  $x = 4\text{Al}$  reacted under normal gravity conditions, (a), (c), (e), (g) and microgravity conditions (b), (d), (f), (h) and for  $x = 9$  conducted under (g) 1g conditions and (h) microgravity conditions.



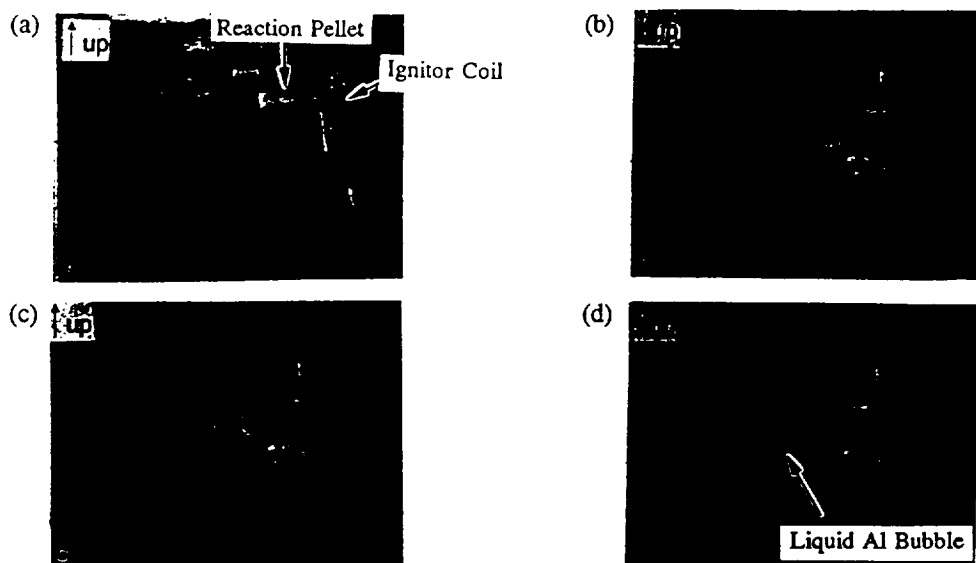


Fig. 8. Video images showing formation of liquid Al droplet forming underneath pellet ahead of reaction front in reaction (2).

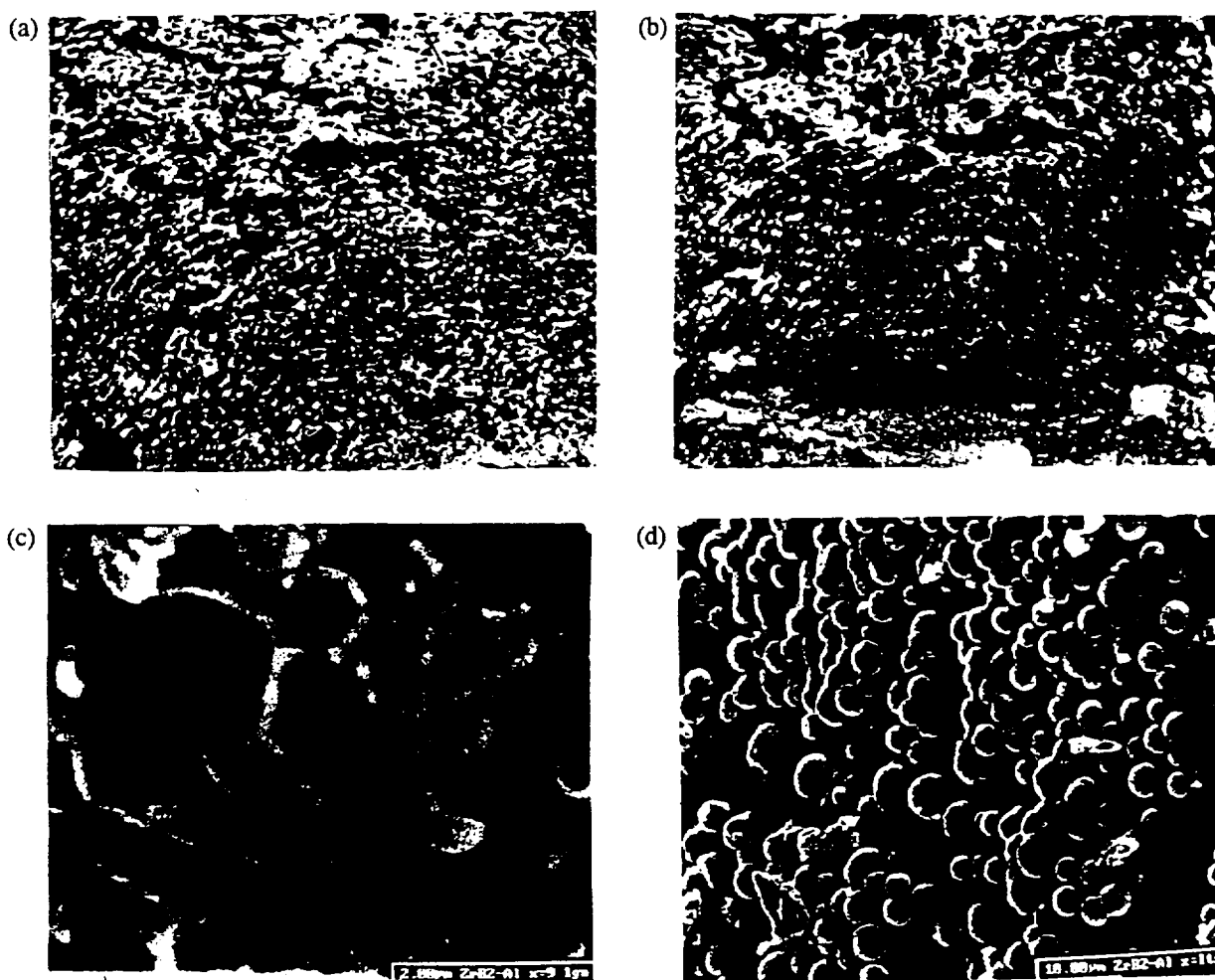


Fig. 9. Macrostructures and microstructures of products for reaction (2) for a reaction stoichiometry  $x = 9\text{Al}$ ; (a) and (c) reacted under microgravity conditions; (b) and (d) reacted under normal gravity conditions.

#### B<sub>4</sub>C-Al<sub>2</sub>O<sub>3</sub>-Al composite system - reaction (3)

Previous research conducted on this reaction<sup>6</sup> under normal (1g) gravity conditions has identified that the combustion temperature is sufficient to produce a single high volume, high pressure B<sub>2</sub>O<sub>3</sub> gas. The extent of this gas generation is sufficient to create a highly porous, e.g. 85% porosity, expanded or "foamed" composite, with expansions of approximately 300% being achieved in the vertical direction on conducting this reaction in the propagating mode

It was not possible to measure ignition temperatures in this reaction system owing to the change in sample and chamber configuration required for these reactions. The effect of reaction stoichiometry (xAl) and gravity on T<sub>c</sub> and the extent of expansion are recorded in Table IV, and the effect of gravity on the degree of expansion is presented in Figure 10.



Fig. 10. Photographs of green pellet for reaction (3) and reaction stoichiometry  $x = 0$ , and reacted samples of this same green pellet conducted under 0g, 1g, and 2g conditions.

It appears that, in this system, T<sub>c</sub> increased on increasing gravity and decreased on increasing the amount of excess Al, while the extent of

expansion decreased on increasing gravity and decreased on increasing xAl.

Increasing gravity will increase the force acting against the expanding gases generated at, and ahead of, the reaction front and therefore, decreases the extent of expansion or "foaming" of this reaction system. Increasing gravity will therefore, decrease the porosity providing a slightly denser material and less heat dissipated into the pores and gases in the pores. This will produce a higher T<sub>c</sub>. Increasing xAl will provide more liquid Al to fill the micropores,<sup>6</sup> resulting in a decreased porosity and decreased expansion. At the same time, increasing xAl will take additional heat out of the porous structure on account of the latent heat of fusion of Al and thereby provide a decrease in T<sub>c</sub>. The differences in microstructure of these expanded composite materials produced under different gravity conditions is presented in Figure 11.

It is apparent that the degree of porosity and uniformity of product particle sizes increases with decrease in gravity [Figure 11(a), (b) and (c)]. In addition, increasing xAl provides a potential source for the synthesis of extremely fine whiskers under microgravity conditions [Figure 11(e)] or needle-like phases under 2g conditions [Figure 11(f)]. It has been established in other combustion synthesis reaction systems that increasing xAl and T<sub>c</sub> in a reaction system involving B<sub>2</sub>O<sub>3</sub> and in which T<sub>c</sub> exceeds 2300°C can provide sufficient volatile species of B<sub>2</sub>O<sub>3</sub> and Al to produce Al<sub>2</sub>O<sub>3</sub> whiskers.<sup>5</sup> Further research, however, is needed in this B<sub>4</sub>C-Al<sub>2</sub>O<sub>3</sub>-Al system reacted under different gravity conditions in order to clearly identify these product phases.

In all three reaction systems, the reactions occurred to completion in the propagating mode for all levels of reaction stoichiometry and conditions of gravity and orientation of the samples. This was verified by x-ray diffraction analysis of the products with no trace of unreacted or partially reacted species being detected.

Table IV - Percent expansions for the B<sub>4</sub>C-Al<sub>2</sub>O<sub>3</sub>-Al reaction system.

System	Percent Expansion			
	x=0	T <sub>c</sub> °C	x=3	T <sub>c</sub> °C
B <sub>4</sub> C-Al <sub>2</sub> O <sub>3</sub> -Al				
1g Conditions	230%	1968	210%	1871
2g Conditions	200%	1975	195%	1876
0g Conditions	320%	1864	290%	1868

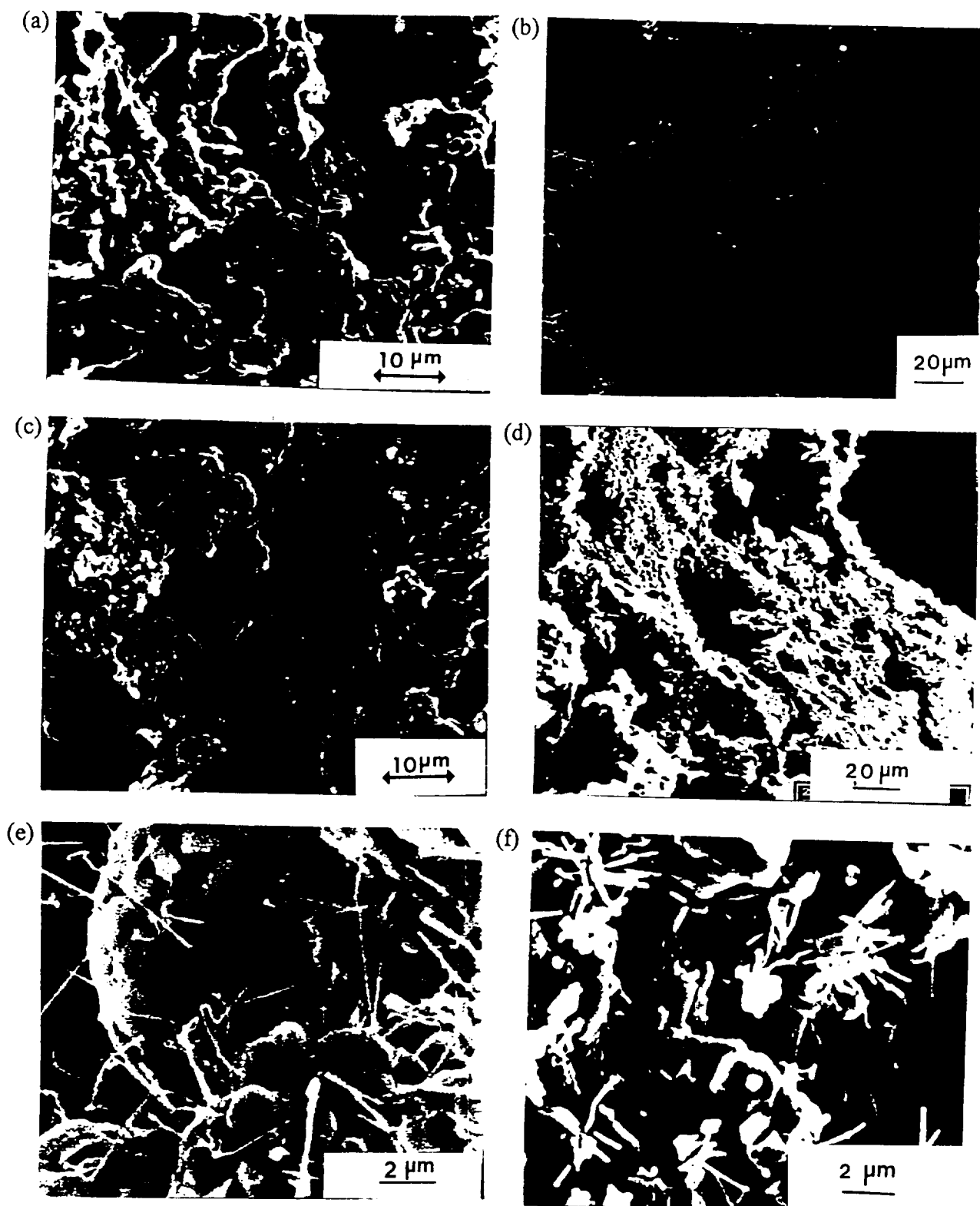


Fig. 11. SEM photomicrographs of products synthesized from reaction (3): (a)  $x = 0$ , reacted under 1g conditions; (b)  $x = 0$ , reacted under microgravity conditions; (c)  $x = 0$ , reacted under 2g conditions; (d)  $x = 3$ , reacted under 1g conditions; (e)  $x = 3$ , reacted under microgravity conditions; (f)  $x = 3$ , reacted under 2g conditions.

### Conclusions

The results from this initial investigation of the effect of gravity on the combustion synthesis of three model reaction systems has clearly indicated that gravitational forces significantly influence the synthesis of composite materials produced by combustion synthesis reactions that generate a liquid and/or gas phase at, or ahead, of the combustion reaction front for reactions conducted in the propagating mode. Conducting such combustion synthesis reactions under microgravity conditions, i.e. in the NASA Lewis Research Center Lear Jet, has resulted in a change in ignition and combustion temperatures and, in some cases a change in propagating velocity; a finer, more uniform distribution of the reactant and product species when a liquid phase, e.g. Al, is generated at the reaction front, and an increased expansion or "foaming" when a single gaseous specie, e.g.  $B_2O_3$ , is generated at the reaction front. The potential for synthesizing fine non-aligned whiskers also appears to be present. In addition, each reaction was completed under microgravity conditions with no unreacted species being detected. Conducting these exothermic reactions under normal gravity conditions resulted in small amounts of unreacted species as identified under x-ray diffraction techniques.

### Acknowledgments

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